DIFFUSION IN SOLID BODIES, TAKING DIFFUSION WELDING INTO CONSIDERATION

S. Rasche

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546   DECEMBER 1974

1. Report No. Nasa 16,059	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Diffusion in solid bodies, taking diffusion welding into consideration.		5. Report Date December 1974
		6. Performing Organization Code
7. Author(s) S. Rasche		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108		11. Contract or Grant No. NASw-2483
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The theoretical principles of diffusion are examined, giving attention to the derivation of the diffusion equation, its solution, the examination of the diffusion coefficient, the temperature dependence of the diffusion coefficient, and the determination of the concentration-dependent diffusion coefficient. Aspects of 'up-hill' diffusion are considered along with the Kirkendall effect and processes involving the presence of various phases. A number of special problems connected with diffusion welding are discussed. The parameters which have to be taken into account in this process include pressure, temperature, welding time, protective atmosphere, and surface roughness. Suitable welding conditions for a number of metal combinations are presented in a table.

17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified - Unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 36	22. Price

DIFFUSION IN SOLID BODIES, TAKING DIFFUSION WELDING INTO CONSIDERATION

S. Rasche

1. Statement of the Problem

Diffusion processes are very important for the technology of production and processing of metals. All heat treatments of steels which produce homogenization or precipitation are based on diffusion processes. Surface treatments, such as case-hardening or nitriding of work pieces are also based on diffusion processes. Recently, diffusion welding has also been used increasingly for joining metallic parts.

By diffusion we mean the process of mixing of unequally distributed molecules of the same or different types. In the simplest case we have an exchange process within one and the same pure material. Then we speak of self-diffusion. This can best be represented and observed as a model in an experiment with a tracer method. This pure form of diffusion, largely free of outside effects, can be described quantitatively by the diffusion equation.

The applicable literature often differentiates between self- and autodiffusion, heterodiffusion and interdiffusion. By heterodiffusion we mean the diffusion of minor impurities. The dosing of semiconductor elements is an example of that. Interdiffusion is the mutual interpenetration of different

---

* Numbers in the margin indicate pagination in the original foreign text.

1

types of atoms across a concentration boundary which is at first
sharp and localizable in space, such as the welding of different
materials [1]. Figure 1 [2] shows the potential diffusions
which occur when a gas diffuses into a crystalline body.
Because of the higher activation energy, the rate of diffusion
is smaller in the interiors of the grains than it is along the
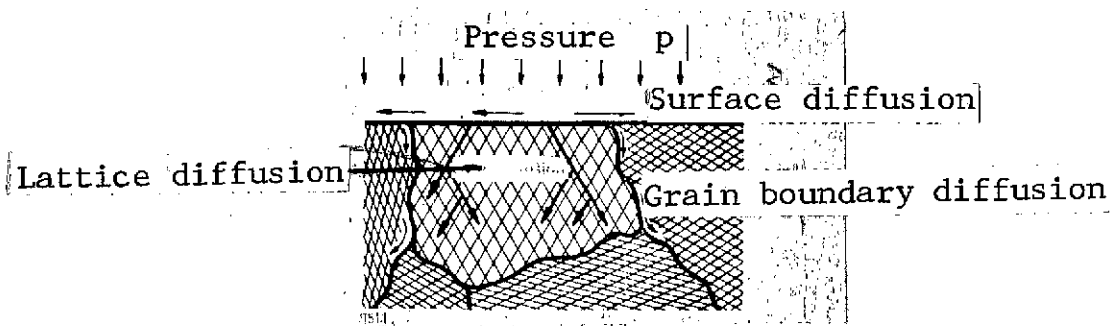grain boundaries and at the surface [2].

Pressure p

Surface diffusion

Lattice diffusion

Grain boundary diffusion

Figure 1. Diffusion at the surface, along the grain boundaries,
and in the crystalline lattice of a material.

2.   Theoretical Principles of Diffusion

2.1   Establishment of the Diffusion Equation

In order to set up the diffusion equation, we consider
a limited volume, V, in which there is a mass, M, of a material.
Due to a process called diffusion in the following, a mass flow,
I, flows out through the surface of this volume. Because of this,
the mass, M, of the material decreases by δt in the time δM.
Then

$$I = -\frac{\delta M}{\delta t} = -\dot{M}.$$

(1)

2

M   mass
I   mass flow
t   time
dV   volume element
c   concentration
C   specific heat
$\vec{dF}$ vectorial surface element
$\vec{m}$ diffusion flux density
D   diffusion coefficient (DK)
$\vec{q}$ heat flux density
κ coefficient of thermal conductivity
T   (absolute) temperature
$\vec{j}$ flux density
σ conductivity coefficient
φ electrical potential
E   electric field strength
Δ = div. grad (Laplace operator)
a   temperature conductivity
ρ density
Q   activation energy
k   Boltzmann constant
B   mobility
x   path of diffusion
$\overline{x^2}$ mean square displacement
C_M Matano concentration
m_i thermodynamic factor

Now if we introduce local quantities and define the mass per unit volume as the concentration, c, and the mass flux per unit area as the diffusion flux density, $\vec{m}$, then we obtain for

$$M(t) = \int_V dV\, c(\vec{m}, t)$$

(2)

and for

$$I = \oint d\vec{F}\, \vec{m} = \int_V dV\, \text{div}\, \vec{m}.$$

(3)

3

We insert Equations (2) and (3) into Equation (1), obtaining

$$\int dV\, (\dot{c} + \text{div }\vec{m}) = 0.$$ (4)

This equation applies for every volume element, dV, of V; the integrand must therefore vanish identically according to

$$\frac{\partial}{\partial t}c + \text{div }\vec{m} = 0.$$ (5)

The equation thus obtained describes the conservation of mass during the diffusion process, so that it is called the continuity equation: The divergence of the mass flux density is exactly equal to the change of concentration with time.

In analogy with Fourier's Solution for the heat flux density, it is usual to introduce a statement for the mass flux density. Fourier's Solution is

$$\vec{q} = -\varkappa\, \text{grad }T.$$ (6a)

Statements of this type can be obtained generally for all the physical phenomena which belong to the family of transport processes (spread of heat, mass, momentum and charge) from the Boltzmann impulse equation. The solution for the diffusion flux density stems from Adolf Fick (1829 to 1901). Fick was concerned with the physical processes in the human body, such as osmosis, which are closely related to diffusion. This solution is

$$\vec{m} = -D\, \text{grad }c.$$ (6b)

This equation is also known as Fick's First Law [3].

4

For completeness, we shall also mention Ohm's law, which describes the transport of charges, and likewise arises from such a solution:

$$\vec{j} = -\sigma \, \mathrm{grad} \, \varphi = \sigma \vec{E}.$$

(6c)

We cannot consider an analogous rule for momentum transport here; see [4] for that.

Fick's Law simultaneously defines the diffusion coefficient, D. But this statement is suitable as an instruction for measurement only in quite special experimental systems, because the other two quantities which appear are only accessible with difficulty for measurement. The diffusion coefficient is reported in cm^2/s and is, as a rule, greater than zero. In this case the diffusion leads to a concentration balance and the mass flux density points in the direction of decreasing concentration. The so-called "up-hill" diffusion with negative D is discussed in the following.

With the statement for the diffusion flux density, Equation (6b), the continuity equation transforms into the diffusion equation according to

$$\frac{\partial}{\partial t} c = \mathrm{div} \{ D \left[c\left(\vec{r}, t\right) \right] \mathrm{grad} \, c \}.$$

(7)

As a rule, the diffusion coefficient depends on the concentration, and thus on the location vector $\vec{r}$ and on the time, t. We can simplify this for constant D, writing

$$\frac{\partial}{\partial t} c = D \, \Delta c.$$

(8a)

This equation is called Fick's Second Law [5]. The temperature equilibration is described by an analogous equation, the heat conduction or thermal diffusion

according to

$$\frac{\partial}{\partial t} T = a \, \Delta T,$$

with $\qquad\qquad\qquad a = \frac{\varkappa}{\varrho C}$ $\qquad\qquad\qquad$ (8a)

Fick's Second Law applies strictly only for self-diffusion.
It also applies approximately at low concentration differences,
and the equation can be utilized for rough calculations, such
as for an approximate determination of the mean diffusion
coefficients. In contrast to Equation (7), this is a linear
partial differential equation, which is a very considerable
simplification. The equation is of the first degree. It is
first-order with time and second-order with respect to the
position coordinates. For its complete solution, therefore,
we must have an initial condition, i. e., a statement of the
state at the time $t = 0$ and two boundary conditions, such as
the complete knowledge of the concentration at the surface of
the region under consideration and the knowledge of the mass
flux through this surface during the experimental period.
These mathematical conditions can also be understood directly
physically.

2.2 Solution of the Diffusion Equation

The solution and the route to the solution for the diffusion
equation are decisively dependent on the boundary conditions.
The mathematically simplest case is that which also occurs as
a rule in diffusion welding. This is the so-called two-fold
infinite half-space. Up to the time $t = 0$ there exists a
sharp boundary with a stepwise concentration drop in the form
of an infinitely extended plane between two half-spaces which
also extend to infinity. This makes the problem one-dimensional
with respect to the position coordinates. Boundary effects do

6

not occur during the experiment. The condition of a sharp
concentration drop at the boundary can be realized particularly
well with solids because of the absence of convection. Because
of the slow course of the diffusion, even relatively small
samples suffice for approximate establishment of the conditions <u>/ 548</u>
of the two-fold infinite diffusion space. For this case, the
diffusion equation takes the form:

$$\frac{\partial}{\partial t} c = D \frac{\partial^2 c}{\partial x^2}$$ (9)

Under these special conditions, the diffusion equation
can be transformed into an ordinary differential equation by
using a solution stemming from Boltzman. For this we set [6]

$$\lambda (c) = \frac{x}{\sqrt{t}}.$$ (10)

This statement selects, from the multiplicity of solutions
to the diffusion equation, those functions which satisfy the
chosen boundary conditions. These are solutions of the form

$$c (x, t) = c (x/\sqrt{t}).$$ (11)

After integration and transformation back to the old
variables, x and t, it follows that:

$$c = A \, \mathrm{erf} \left(\frac{x}{2 \sqrt{D} \, t} \right) + B$$ (-r)

with

$$\mathrm{erf} (\xi) = \frac{2}{\sqrt{\pi}} \int_0^\xi \exp (-\varrho^2) \, d\varrho = 1 - \mathrm{erfc} (\xi)$$ (..)

and

$$\xi = \frac{x}{2 \sqrt{Dt}}$$ (12)

7

The two integration constants, A and B, are determined from the initial conditions. Let the initial concentration, c_0, prevail in the region $x < 0$ at the time $t = 0$, and in the region $x > 0$, let $c = 0$. With this, after a brief calculation, one obtains

$$c = \frac{c_0}{2} \text{erfc} \left(\frac{x}{2 \sqrt{D t}} \right).$$ (13)

At the point $x = 0$, we have half the initial concentration at all times, t.

Figure 2 [7] shows the relations with slightly generalized boundary conditions. At the time $t = 0$, the initial concentration, c_0, prevails at the left of the diffusion plane, $x = 0$, and the concentration c_1 at the right of it. For $c_1 = 0$ the equation transforms into the Equation (13) which was just found. Two solution curves are plotted for successive times $t_2 > t_1$. These curves may be linearized on probability paper having its ordinate divided according to the Gaussian integral.
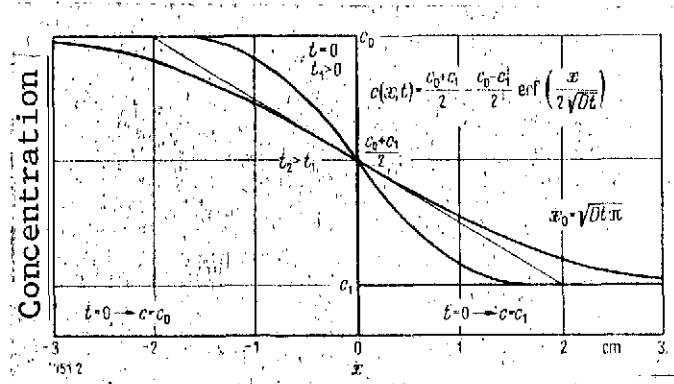

Figure 2. Solution of the diffusion equation for the two-fold infinite half-space.

2.3 Estimation of the Diffusion Coefficient

In diffusion experiments, the mean displacement of the atoms can often be estimated approximately as the visual penetration depth in a polished metallographic section. If only a rough reference value for the diffusion coefficient (DK) is of interest in such a case, we can avoid solving Equation (13) for D and the time-consuming determination of the trios (c; x; t). As the diffusion coefficient in the region accessible to experimental investigations can vary by some 12 to 14 orders of magnitude, even quite crude estimates are often extremely valuable [2].

The so-called mean square displacement is equal to the mean of the squares of all the displacements, x, which the diffusing particles have experienced up to time t [5]. If we consider one single particle of the totality, then the square root of the mean square displacement is the statistically expected value for the particle position at the time, t, according to

$$\overline{x^2(t)} = \frac{\int\limits_{-\infty}^{\infty} x^2 c\,(x,\,t)\,dx}{\int\limits_{-\infty}^{\infty} c\,(x,\,t)\,dx} \tag{14}$$

The concentration, c, which occurs in the numerator as the nucleus is the statistical weighting function of the distribution.

If the diffusion material departs from the initial condition just discussed, lying as a thin layer at the surface of matrix under consideration, then in place of Equation (13) we have a simpler solution

$$c\,(x,\,t) = \frac{1}{\sqrt{\pi\,D\,t}} \exp\left(\frac{-x^2}{4\,D\,t}\right) \tag{15}$$

In this way, we obtain from the evaluation of the defining equation (14) for the mean square displacement the relation well known from the literature [2, 5]

$$\overline{x^2} = 2Dt.$$

(16)

By definition, $\sqrt{\overline{x^2}}$ is the width of the distribution.

If, on the other hand, we calculate the mean square displacement by inserting Equation (13) into Equation (14) for the two-fold infinite half-space, then, departing from Equation (16), it follows that

$$\overline{x^2} = \frac{4}{3}Dt.$$

(17)

Using these equations, one can already undertake a rough estimation of the diffusion coefficient from the metallographic finding.

For more accurate determination of the diffusion coefficient, we solve Equation (13) or Equation (15) for D. This, to be sure, leads to transcendental equations, and therefore must be carried out with graphical or iterative methods.

For this, we must first determine experimentally the concentration distribution. It is convenient to do this with an electron beam microprobe [7, 8]. It is also necessary to insure that the assumption of a concentration-independent diffusion coefficient is met. This can be done by testing the linearity of the distribution on probability paper.

In this respect, let us for completeness refer to a very well known equation stated by A. Einstein in 1905. The

10

Einstein relation gives a relation between the diffusion constant and the so-called mobility. By mobility, B, we mean generally the proportionality constant between the force, K, causing motion of an arbitrary particle and the resulting particle velocity, v, [5] by the relation

$$v = B K. \tag{18}$$

The Einstein relation, then, is

$$D = B k T. \tag{19}$$

where k is the Boltzmann constant and T is the absolute temperature.

This relation has great significance for modern electrotechnology, especially for the most important effects occurring in semiconductor physics, which are essentially determined by charge carrier diffusion.

In order to avoid systematic errors in diffusion studies, it is desirable to test the relation

$$x(c,t) \sim \sqrt{t}. \tag{20}$$

We also did this in our own studies. The initial /549 pieces for the samples used consisted of one cube of Armco iron and one cube of pure nickel. Polished surfaces of each were clamped together in a screw clamp. The diffusion heating was done for 24, 48 and 72 hours at 1,000°C in a reducing hydrogen atmosphere. The samples which were welded together in this way were then separated by a cut perpendicular to the plane of the weld, and the cut surfaces were polished. The sections thus obtained could be used for studies of the course of diffusion by means of electron beam microanalysis.
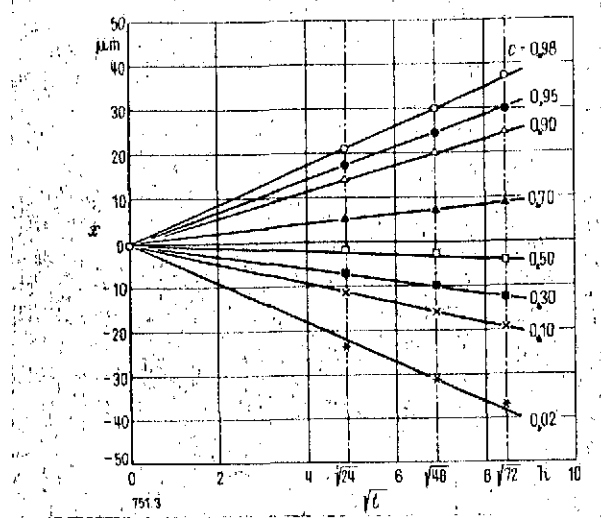
Figure 3. Demonstration of an undisturbed course of diffusion.

Figure 3 [7] shows the spatial migration of fixed concentration steps as a function of the square root of the diffusion time. This relation must be strictly linear.

2.4 The Temperature Dependence of the Diffusion Coefficients

The temperature dependence of the diffusion coefficient can be represented by

$$D = D_0 \exp(-Q/kT) \tag{21}$$

Here Q is the activation energy of the process. In order for an atom to change its place, it must first exceed the potential threshold caused by its neighbors. D_0 is the theoretical diffusion coefficient which would occur at infinitely high temperatures or various activation energies, respectively.

12

Table 1 [2] contains a summary of the results of various authors in order to demonstrate the orders of magnitude of the diffusion coefficients. The highest diffusion rates can be expected for the migration of carbon in iron.

Table 1. VALUES OF SOME DIFFUSION COEFFICIENTS. MATERIAL A MIGRATES INTO MATERIAL B.*

A	B	T K	D cm²s⁻¹	D_0 cm²s⁻¹	Q cal *)	$\sqrt{\bar{x}^2}$ *) µm
Cu	Ag	600	$7,72 \cdot 10^{-16}$	$2,9 \cdot 10^{-2}$	94 800	10^{-3}
Fe	Fe	1 112	$5,2 \cdot 10^{-13}$	$1,04 \cdot 10^{-3}$		$2,6 \cdot 10^{-2}$
Fe	Ni	1 200	$9,3 \cdot 10^{-11}$			9,35
Cu	Ni	950	$2,1 \cdot 10^{-10}$	$6,5 \cdot 10^{-5}$	29 800	0,53
Ni	Cu	890	$2,4 \cdot 10^{-10}$	$1,04 \cdot 10^{-3}$	35 500	0,57
Al	Cu	565	$1,3 \cdot 10^{-9}$	$8,4 \cdot 10^{-2}$	32 600	1,3
Fe	Al	1 050	$2,0 \cdot 10^{-8}$		44 000	5,2
Cu	Cu	1 000	$4,7 \cdot 10^{-8}$	70	56 000	7,9
C	Fe	1 100	$1,2 \cdot 10^{-6}$			40

*) 1 cal = 4,19 J
*) t = 10 s; Gl. (17)

*Translator's note: Commas in numbers represent decimal points.

2.5 The Determination of a Concentration-Dependent Diffusion Coefficient

As a rule, the diffusion coefficient is concentration-dependent. This can be neglected only at low alloy concentrations. This is detected by asymmetries which appear in the concentration curve. Here, it is convenient to transform the concentration curve into a probability plot. If this does not give a straight line, then the diffusion coefficient must be determined by a method which was first presented by the Japanese, C. Matano [9] in 1933. The plot of the measured

points on probability paper not only determines immediately
whether the diffusion coefficient depends on the concentration,
but it also allows a certain compensation for the scattering of
the measurements [2]. Figure 4 [7] shows our own experimental
results. As there is obviously not a straight line in a
probability plot, the diffusion coefficient in the system
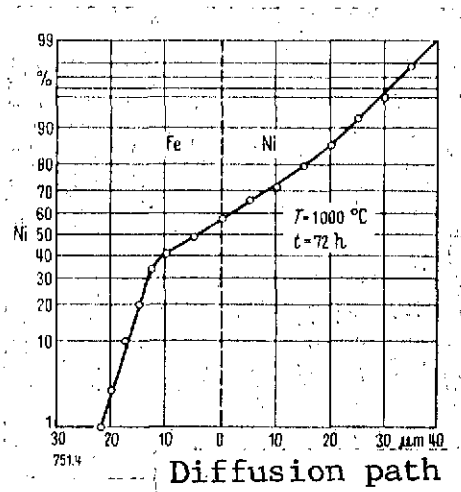iron-nickel is concentration-dependent.

Figure 4. Diffusion curve with a diffusion coefficient which
is significantly dependent on the concentration.

The ordinate is divided according to the Gaussian
integral ("probability paper"). The percentages
reported refer to the atomic weight.

For this case, and this is the usual case, the diffusion
coefficient also depends on the position coordinate, so that
the transformation from Equation (7) to Equation (8) cannot be
performed. For the general case of the two-fold infinite
halfspace treated here, Equation (7) takes on the following
form:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right).$$

(22)

14

By use of the Boltzmann solution, $\lambda = x/\sqrt{t}$, one obtains after single integration and appropriate transformation an expression for the diffusion coefficient:

$$D(c') = -\frac{1}{2\,t_0}\frac{dx}{dc'} \int_0^{c'} x\,dc.$$ (23)

At the point of the zero of the abscissa, x = 0, which previously coincided with the position of the welding plane, there appears here the position of the so-called Matano plane, which must not be identical with the original weld plane. This is related to the fact that the lattice parameter can alter significantly over an alloy composition range of 0 to 100%. If the concentration C = C_M is assigned to the new coordinate origin, then (Matano condition) we have

$$\int_0^{C_M} x\,dc + \int_{C_M} x\,dc = 0.$$ (24)

The equation requires establishment of the Matano plane in the form such that both the triangular surface segments between the measured curve and the plane x = 0 have the same area, Figure 5 [7].

In order to evaluate Equation (23), we obtain the value of dx/dc and the matching value for the integral graphically, after having established the plane x = 0 planimetrically according to the Matano condition.

Because of the lattice expansion which occurs with increasing concentration of alloys and the reduction of the melting temperature generally linked with that, one often finds a close relation between the course of the liquidus line and the course of the concentration dependence of the diffusion coefficient. Figure 6 [7] shows the diffusion coefficient measured in the Fe-Ni system investigated. Generally, as is the case here, one finds the diffusion coefficient rising with decreasing melting temperature.
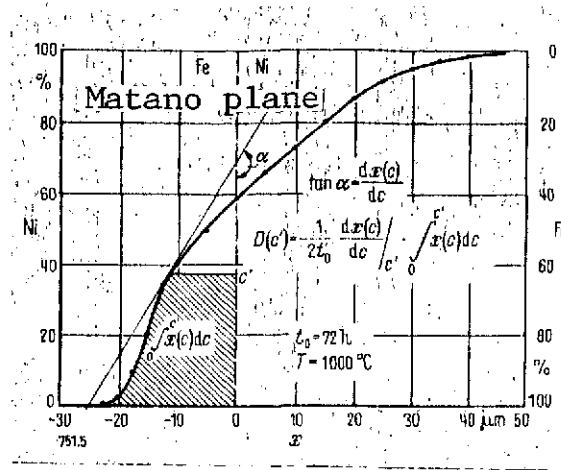
15

Figure 5. Example of the Matano evaluation of a Ni-Fe diffusion sample.
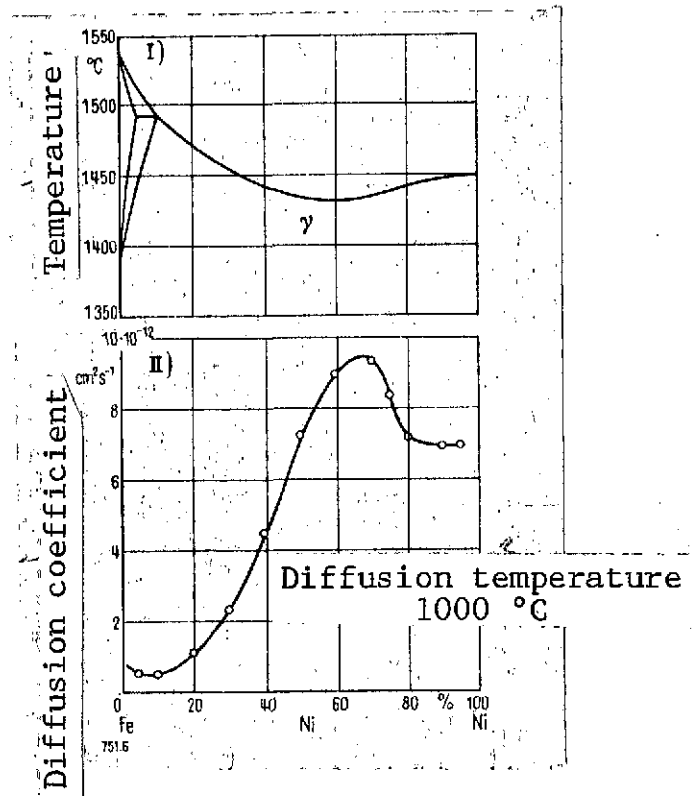

Figure 6. Relation between the liquidus line and the measured course of the diffusion coefficient in the Fe-Ni system. (I) Liquidus line in the Fe-Ni system (II) measured course of the diffusion coefficient. The percentages refer to the atomic weight.

16

# 3. Various Special Effects

3.1 "Up-hill" Diffusion

At low concentration differences, in particular, the concentration gradient appears to be the driving force, so to speak, for the diffusion which occurs. But in fact there is a superior viewpoint according to which the diffusion leads to a state of minimal free enthalpy. The diffusion flux density is, therefore, proportional to the gradient of the activity. Only in the case of an ideal solution does this correspond to Fick's statement.

In 1932, L. Onsager first reported, in describing diffusion in aqueous electrolytes, that Fick's law should contain the activity in place of the concentration, as it is not a concentration gradient but solely the striving for thermodynamic equilibrium which is the cause of an equilibration process.

U. Dehlinger transferred this concept to alloys. Later, L. S. Darken worked on the same problem. Starting with the chemical potential, he developed the form of the thermodynamic factor, m, which is generally used today. This is the factor by which the diffusion constant must be expanded:

$$D = D' m_i.$$

(25)

The thermodynamic factor, m_i, expresses the deviation of a system from Henry's Law. If there are binding forces between the diffusing components and the other portions of the alloy, then $m_i > 1$. With repulsive forces, $m_i < 1$. As soon as $m_i < 0$, there is diffusion against the concentration gradient [10].
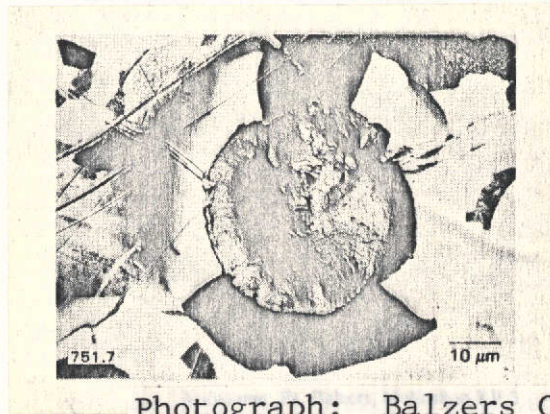
Figure 7. Photoemission picture of spheroidal graphite iron.

One speaks of the region of negative or "up-hill" diffusion.
In practice, there are many examples of this, such as precip-
itation processes in supersaturated solid solutions. One example
is the development of graphite spheres (spheroidal graphite iron),
Figure 7, or lamella in gray cast iron. The separated carbon,
at first diffuse, deposits on existing nuclei. From the
centers thus formed, regular graphite spheres arise through
"up-hill" diffusion. These are surrounded by a sharply delimited
depletion zone, a so-called ferrite border.

In two-component alloys, "up-hill" diffusion is possible
only in demixing processes, such as nucleation. Particularly
interesting conditions appear in interstitial solid solutions,
because the interstitial components show mobility higher by
several orders of magnitude than do the other components of
the alloy, due to their preferred position in the lattice,
as a rule. In this relation, L. S. Darken studied the separation
of cementite from austenite supersaturated with carbon, where
diffusion occurred against the concentration gradient [10].

18

3.2   Occurrence of Several Phases

Most metals form intermetallic phases with each other, so that diffusion between two partners often proceeds through several phases.   The course of diffusion is determined here by the different diffusion coefficients of the phases which occur and by their growth rate.   The characteristic polished section picture of the diffusion zone is particularly characterized by the fact that the phases which occur appear as zones sharply delimited from each other.   This characteristic layer formation,   Figure 8,   can usually be shown through suitable etching of the polished section, Figures 9 to 12 [2, 11, 12].   The dependence of the width of the diffusion
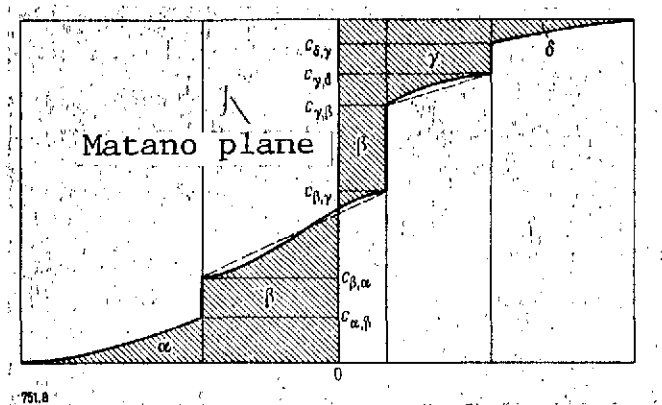
Figure 8.   Diffusion with development of several phases.

zones which appear in the metallographic polished sections (intermatallic phase Fe-Al) on the diffusion time, to be sure, strikingly contradict the statements made about Equation (20) and Figure 3.   These dependences are seen in Figures 10 and 12 from [13] and [14] and in a private communication from the Central Institute for Reactor Experiments of the Jülich Nuclear Research Establishment, Jülich.   Here, instead of Equation (20) we apparently have $x \sim \exp(t/t_0)$, which simulates an extremely progressive character of the diffusion process.

Figures 9 and 10:   Diffusion zones and their growth during
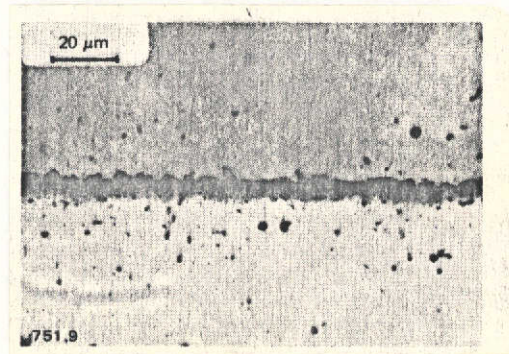   diffusion welding.

Figure 9.   Diffusion zone of the compound X 10 CrNiTi 18 9-
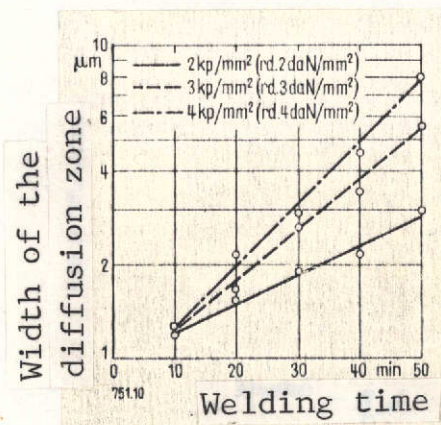 $AlMg_3$ with several intermetallic phases.

Figure 10.   Growth of the diffusion zone in Figure 9 as a
             function of the time and of the applied pressure.
             Welding temperature T = 500°C.

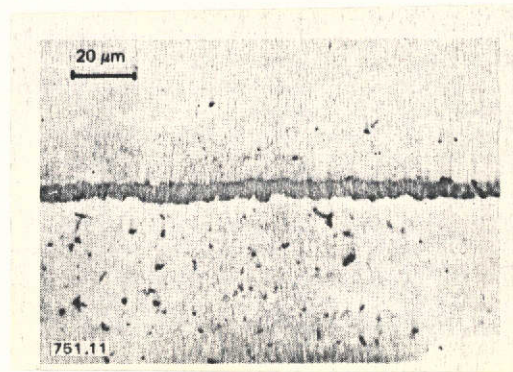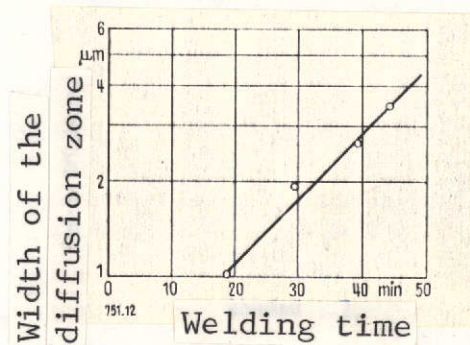Figures 11 and 12.   Diffusion zones and their growth during
diffusion welding.

Figure 11.   Diffusion zone of the compound X 10 CrNiTi 18 9 -
Al 99.8 with a single intermetallic phase.

Figure 12.   Growth of the diffusion zone in Figure 11 as a
function of the time at a welding pressure of
4 kp/mm^2 (about 4 daN/mm^2). Welding temperature
T = 500°C.

The originally exponential course (straight lines with logarithmically divided ordinates in Figures 10 and 12) may, however, be explained as follows: Ideal metallic boundaries are not present at the beginning of the welding process, and the initial and boundary conditions used in deriving Equation (17) (sharp, plane boundary with intimate contact of the components, one-dimensional problem) are not fulfilled. Initially there is only point contact of the surfaces to be welded. The existing roughness peaks are degraded by growth processes. Only when complete contact of the two components occurs at the boundary will the straight lines mentioned bend, and exponential growth of the diffusion zone will transform approximately into growth according to Equation (17). The contradiction between Figure 3 and Figures 10 and 12 is, then, possibly soluble by different sample preparation. The experimental proof is reserved for further experiments.

3.3 Kirkendall Effect

An effect which was first found by E. O. Kirkendall in the diffusion of Cu versus α-brass, and later found in other cases by W. Seith, directly shows the action of holes in the lattice on diffusion. This Kirkendall Effect is that during diffusion the previously marked boundary of the Cu-rich crystal shifts markedly toward the Zn-rich brass. Thus, the diffusion flux of the Zn into the Cu-rich crystal is greater than the opposing flow of the Cu. This shows that the Cu and Zn atoms first change places with holes. That is, holes and atoms migrate oppositely. Here it must be assumed that the Zn atoms jump more quickly into an adjacent hole than do the Cu atoms [2, 15].

The Effect also occurs in the silver-gold combination, and leads to hole development in the silver component. At the same time there is a narrowing on one side and development of a bulge on the other side (Figure 13 [2]). The Kirkendall Effect can sensitively disturb the development of a weld at longer diffusion times.
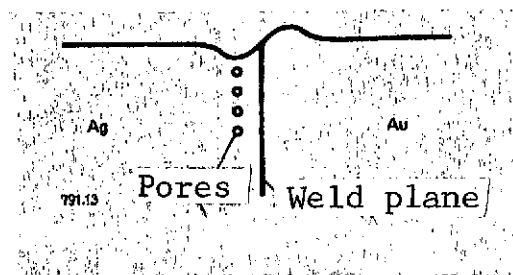
Figure 13. Bulge, narrowing, and pore formation in the diffusion welding of silver and gold.

4. Special Problems of Diffusion Welding

Diffusion welding is joining of work pieces in the solid state. The joining of the roughness peaks in contact is produced through diffusion with a minimum of macroscopic deformation. The diffusion proceeds through application of heat and pressure in a limited time interval under vacuum or protective gas [16]. This definition of the process, based on DIN 1910, contains all the parameters which appear:

1. the pressure
2. the temperature
3. the welding time
4. the protective atmosphere, and
5. the surface roughness.

The required pressures are between 0.5 and 10 kp/mm^2 (0.5 and 10 daN/mm^2). The temperature is usually taken as 70% of the lower of the melting temperatures, in degrees Celsius. The diffusion times needed for production of useful combinations are between 10 minutes and several hours. As the protective atmosphere, a high vacuum of better than 10^{-5} torr (1 torr = 1.33 · 10^{-3} bar) is usually used. This is also unconditionally necessary because of the long diffusion times. As a rule, highly purified protective gases are not used, because the welding chamber must likewise be pumped out to this value before flooding. Table 2 [16] shows some acceptable parameter combinations.

Table 2. PARAMETER EXAMPLES FOR DIFFUSION WELDING.

Material I	Material II	Interlayer	T °C	p daN/mm^2	t min
Copper	Steel		900	0,5	10
Copper	Nickel		900	1,5	20
Copper	Copper		800 to 850	0,5 to 0,7	15 to 20
Titanium	Nickel		800	1,0	10
Titanium	Copper	Niobium	950	0,5	30
Molybdenum	Molybdenum	Titanium	915	700	20
Molybdenum	Steel		1 200	0,5	10
Tungsten	Tungsten	Niobium	925	700	20
Zircaloy-2	Zircaloy-2	Copper	1 040	2,1	30 to 120
Kovar	Kovar		1 000 to 1 110	2,5 to 2,0	20 to 25
Steel	Aluminum		500	0,75	30

Sample preparation is difficult, because roughness depths in the micrometer range are required. This presupposes lapping or polishing of the joining surfaces. This often leads to an undesired crowning of the sample surfaces.

design of diffusion welding equipment follows directly from the requirements mentioned. There must be a vacuum chamber which can be evacuated by a controlled pump system (vane pump, Roots pump, oil diffusion pump). Inside this is the specimen holder, a hydraulic system to produce the welding pressure, and a system for electrical heating of the work piece, as well as a coating arrangement, Figure 14 [13].

The heating must be very even, so that it is convenient to place an induction coil about the joint in the work pieces and operate with high or medium frequency. With smaller work piece cross sections, conductive heating is also possible. Figure 15 gives an impression of the size of the equipment.

As the joining occurs initially through the roughness peaks, it can happen that the points not in direct contact are not completely filled, leaving pores. Such cavities can be avoided by increasing the welding pressure and/or the temperature. Another method, which is at present being perfected, is the use of thin intermediate foils of highly pure and therefore soft metals which can flow into these initial hollows. These layers should be so thin that they are alloyed out of the work pieces to be welded by diffusion, so that they cannot be weak points in the welded joint. By insertion of an interlayer of a metal which diffuses faster into the work materials to be joined than / 553 they diffuse into each other, one can also accelerate the welding. Brittle intermetallic phases which may form between work pieces without an interlayer can also be avoided.

The so-called autobrazing is an interesting variant of diffusion welding. Here the two materials to be joined form a low-melting eutectic in the weld plane by diffusion. The melting point of the eutectic is below the welding temperature [16, 17].
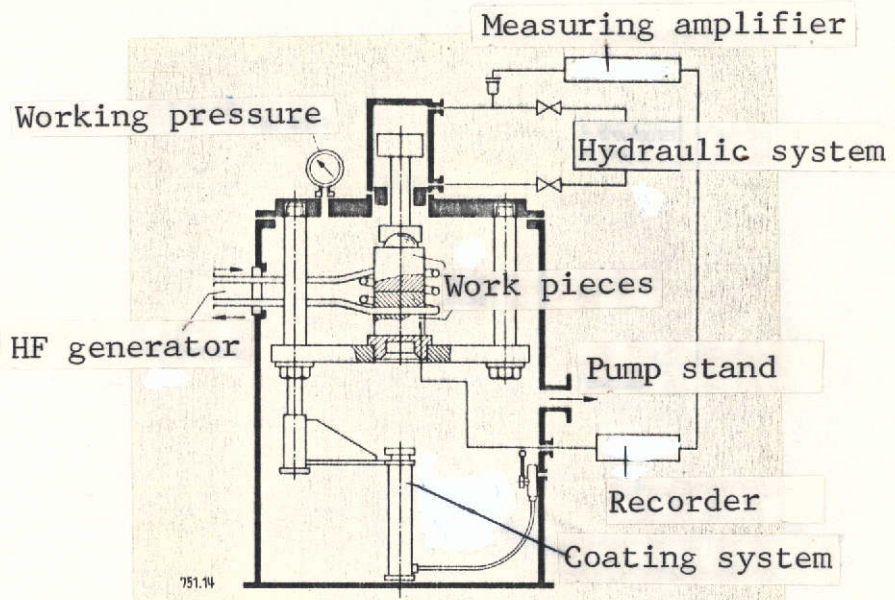
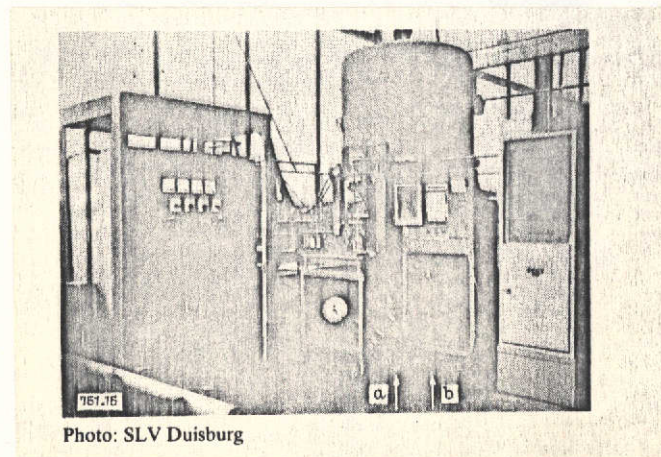Figure 14.   Structure of a diffusion welding device.

Photo: SLV Duisburg

Figure 15.   Diffusion welding system.
              System with conductive (a) and inductive (b)
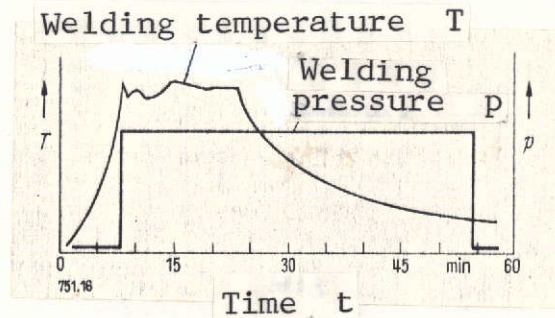   heating of the work pieces.

26

Figure 16. Time course of the welding temperature and welding
pressure in diffusion welding (schematic).
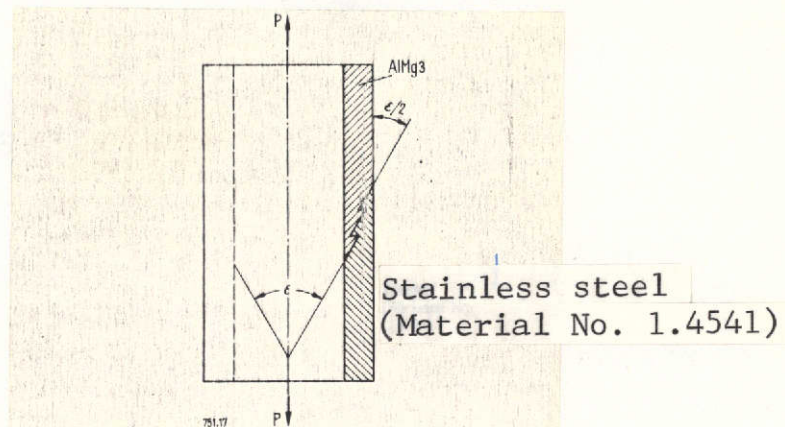Weld temperature T = 500°C
Weld pressure p = 3 daN/mm^2.

Figure 17. Section through a diffusion weld.
The aluminum alloy flows behind the conical steps
prepared in the steel part during the welding
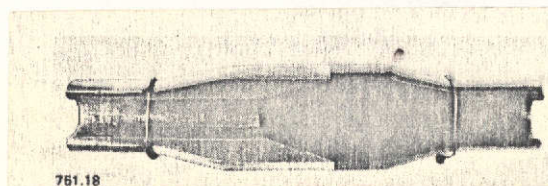process, forming a form-sealed positive bond.

Figure 18. Section of a finished welded part. The part is
bored out and finish-turned.

27

At the Jülich Nuclear Research Station (Central Institute
for Reactor Experiments) bonds between aluminum and steel are
necessary in the insertion capsules for reactor experiments
[13, 14]. Aluminum was chosen as a material for thermal and
neutron-economic reasons. Aluminum and steel cannot be welded
by the usual methods because the two materials form a brittle
intermetallic phase. For this welding problem, therefore,
a combination of flow-pressing and diffusion welding was chosen.
Through appropriate sample preparation, one gets a form-sealed
bond through mutual serrations in the work pieces. Stresses
which occur need not, therefore, be taken up only by the welded
joint (Figures 16 to 19).

In general, diffusion does not appear to have the great
importance for the development of a defect-free welded joint
which the literature often ascribes to it, because the atoms
or groups of atoms diffusing over the boundary surfaces do not
retain any sort of connection to their old lattice site, and
"intermeshing" in this way is impossible. The origin of a new
structure in the vicinity of the joined surface through
recrystallization and epitaxial grain growth across the grain
boundaries is much more important.

This did not occur with the austenitic diffusion welding
sample shown in Figure 20. The original joint surface can still
be recognized distinctly. The microhardness test which was done
shows no change in the original properties of the structures.
Only in the weld plane itself can a drop in hardness be seen.
Figure 21 shows a perlitic-ferritic weld sample. Here the weld
plane is almost completely integrated into overlapping grains. /554
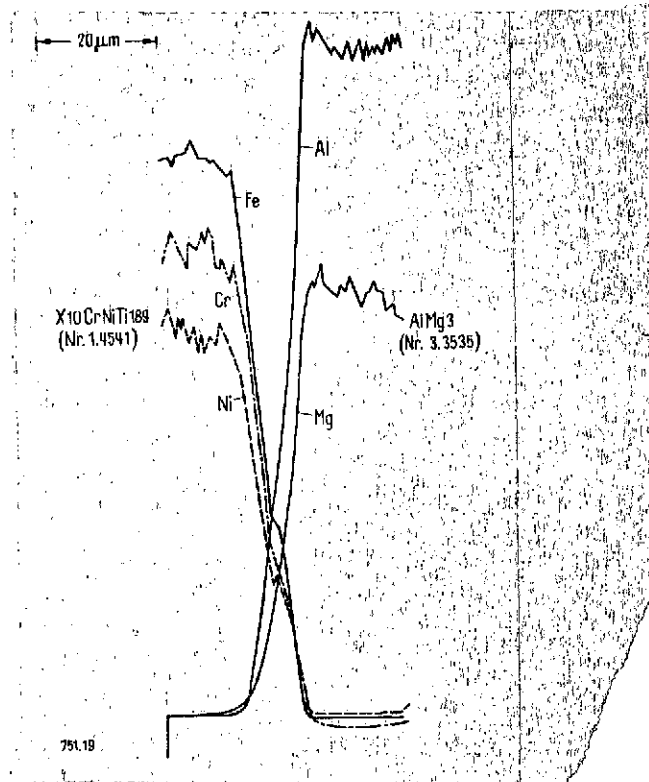This is also confirmed by the hardness test.

Figure 19. Qualitative analysis of the diffusion zone
(intermetallic phase) of a welded bond between
X 10 CrNiTi 18 9 and AlMg 3 using the electron
beam microprobe.

With a titanium sample, Figure 22, the weld plane has
completely merged into the original structure and cannot be
detected any longer, even under the electron microscope. The
hardness test also allows hardly any conclusion to be made
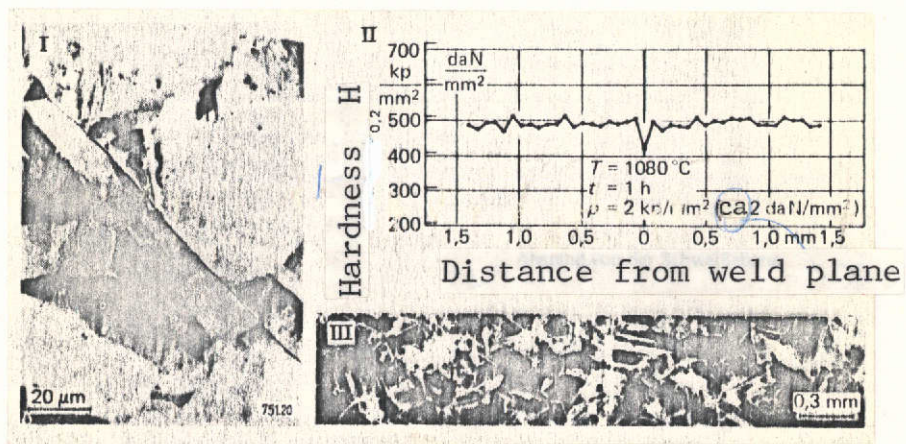about the position of the joining surface.

Figure 20. Electron microscopic picture of the structure in a diffusion-welded joint in austenitic steel and the result of the hardness test.

Material analysis: C = 0.04%; Mn = 2%; Si = 1%; Ni = 10%; Cr = 18%; remainder Fe.
I. Structure picture.
II. Hardness of the bond as a function of the distance from the weld plane.
III. Structure picture with the impressions from hardness testing.

Photograph: Institute for Welding Technology Manufacturing Methods, Aachen Technical College (ISF); Metioskop KE 3.

Even if the welding goes satisfactorily in the interior of the sample, there are usually problems at the edges. This is particularly true in joining different materials, as Figure 23 shows.

This is a bond of a carbon steel with cast iron. Here the joining surface can still be detected only at the edge. This, of course, leads to dynamic stresses on the work piece because the notch effect leads to initiation of cracks. Therefore, and because of the plastic deformation of the cast piece, after-working is necessary.
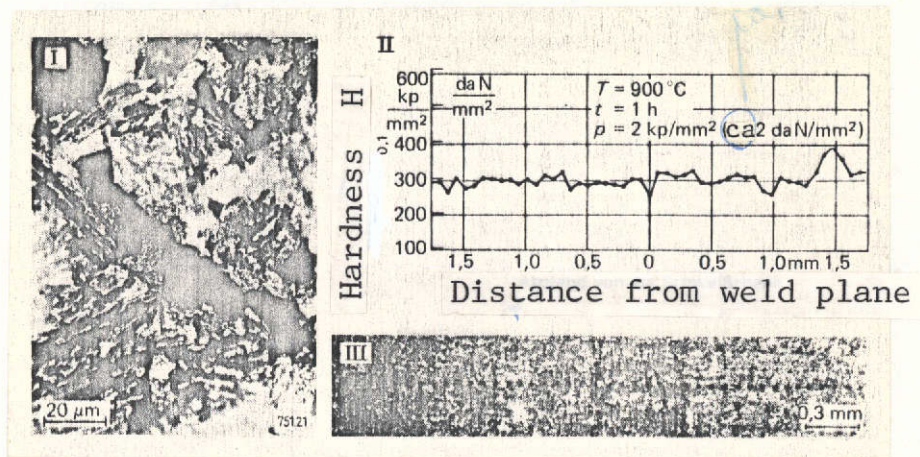
30

Figure 21. Electron microscopic structure picture from a diffusion welded joint of low-alloy steel and the result of the hardness test.
Material analysis: C = 0.25%; Mn = 0.8%; Si = 0.2%; Cr = 1.1%; Mo = 0.2%; Ni = 0.3%, remainder Fe.
I. Structure picture. II. Hardness of the joint as a function of the distance from the weld plane.
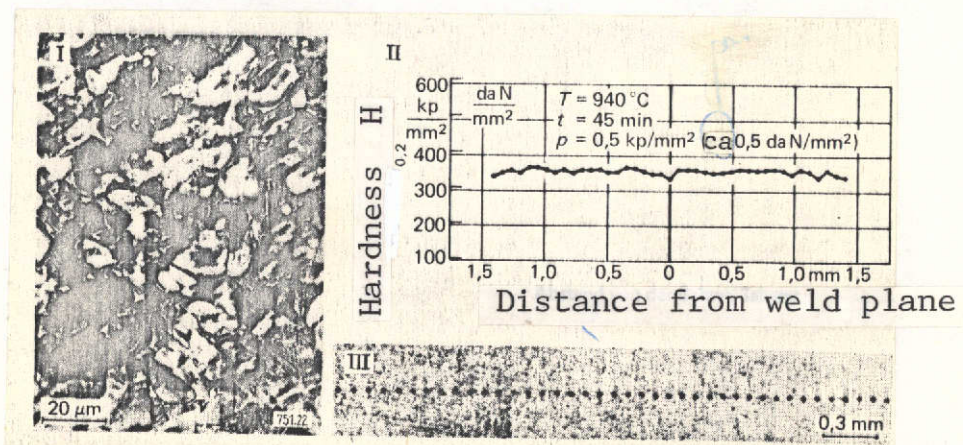III. Structure picture with impressions from hardness testing.

Figure 22. Electron microscopic structure picture from a diffusion welded joint of titanium and result of hardness test.
Material analysis: Al = 6%; V = 4.2%; Fe = 0.3%; C = 0.8%, remainder Ti.
I. Structure picture. II. Hardness of the joint as a function of the distance from the weld plane. III. Structure picture with hardness testing impressions.

Photos: Institute for Welding Techniques of the Technical University, Aachen.
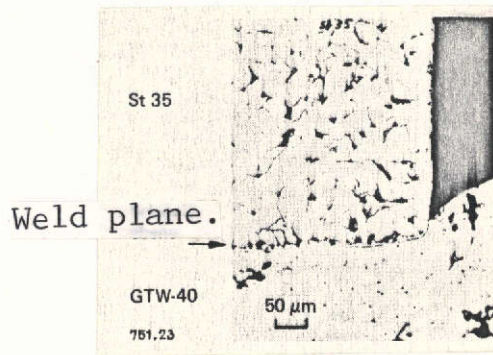
31

Figure 23.   Problems at the edge of the joint between steel St 35
and cast iron GTW 40.

Also, there is no kind of non-destructive test method
for diffusion-welded joints, such as are regularly required
by the acceptance organizations. The very fine joint and any
defects in it are not shown either by ultrasonic testing or
by X-ray examination. For these reasons, and because of the
long welding times and the expensive sample preparation,
diffusion welding will remain limited to special air and space
applications, to semiconductor production, and to reactor
technology. It will not displace existing bonding techniques
there, but will open up new and interesting potentials with
respect to design and material selection.

REFERENCES

1. Théler, J. J.   Interdiffusion and kinetics of precipitation in aluminum-manganese alloys in the presence of iron.   Schweizer Arch. Vol. 38, No. 12, 1972, pp. 422 - 448.

2. Seith, W.   Diffusion in metals.   Berlin: Springer Verlag, 1955.

3. Fick, A.   Ann. Phys. Vol. 94, 1855, p. 59.

4. Sommerfeld, A.   Mechanics of deformable media. Lectures on theoretical physics.   Leipzig: Akad. Verlagsges., 1964, p. 64.

5. Becker, R.   Theory of heat. Berlin: Springer-Verlag, 1966.

6. Boltzmann, L.   Ann. Phys. (NF)   Vol. 53, 1894, p. 959.

7. Huwer, W. and S. Rasche.   Investigation of diffusion processes through the boundaries in plasma-coated welds.   Unpublished work from the Institute for Welding Technology Manufacturing Methods, Aachen, 1970.

8. Bergner, D.   On the measurement of small diffusion coefficients with the microprobe.   Microchimica Acta (Vienna) Suppl. III, 1968, pp. 19 - 26.

9. Matano, C.   Jap. J. Phys. Vol. 8, 1933, p. 109.

10. Wever, H. and H. Flender.   The "uphill" diffusion of carbon in single-phase and multiphase iron-carbon alloys.   Arch. Eisenhüttenwes. Vol. 35, No. 1, 1964, pp. 65 - 73.

11. Niemann, J. T. et. al.   Diffusion Bonding below 1000°F.   Welding Research Suppl., No. 8, 1968, pp. 337s - 342s.

12. Rehme, H.   Observation of diffusion processes with the emission electron microscope.   Z. Metallkde. Vol. 56, No. 2, 1965, pp. 84 - 92.

13. Lison, R.   Diffusion welding and its application. Examples from nuclear technology.   Schweissen u. Schneiden, Vol. 23, No. 8, 1971, pp. 304 - 308.

14. Lehrheuer, W.   Diffusion welding of austenitic chromium-nickel steels with aluminum.   Kerntechn. Vol. 10, No. 4, 1968, pp. 208 - 213.

15.   Smigelskas, A. D. and E. O. Kirkendall.   Trans. AIME
          Techn. Publikat. No. 2071, 1946.

16.   Gerken, J. M. and W. A. Owczarski.   A Review of Dif-
          fusion Welding.   Welding Research J., No. 109, 1965.

17.   Horn, V.   Diffusion welding - a new joining method.
          ZIS-Mitt. Vol. 5, No. 4, 1963, pp. 580 - 586.